Chapter 24

Heavy Metal Deposition in Soils and Plants Impacted by Anthropogenic Modification of Two Sites in the Sudan Savanna of North Western Nigeria

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Additional information is available at the end of the chapter

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1. Introduction

Heavy metals occur naturally in the ecosystem, most of them in trace quantities [1]. Depending on their concentration, some of them like Zn, Fe, Mn and Cu are essential plant nutrients [2, 3, 4], others like Pb, Hg and Cr do not have any known use to plants.

Deposition of heavy metals in soils from anthropogenic activities have been implicated for an increase in heavy metal concentration above background and recommended levels [5, 6, 7]. Heavy metals are important components of agro-allied products such as pesticides, herbicides, fertilizers; manufacturing and other synthetic products such as paints and batteries [8]. Mining activities, industrial, municipal and domestic wastes have been reported to be important sources of heavy metal pollution to the environment [9].

Combustion of fuel from petroleum, abrasion of tyres, brake lining, corrosion of the body work of vehicles and engine wear have been associated with elevated concentrations of Cd, Cu, Mn, Ni, V and Zn [10, 11, 12, 13].

Excessive concentration of heavy metals in the environment is of great concern because of their non-biodegradability. Therefore, their persistence in the environment portends health hazard to plants and animals and consequently trigger ecological imbalance in the ecosystem [14]. Another concern that high concentrations of heavy metals raise is their ability to bioaccumulate across the food chain, with members that are high up the food chain having concentration of such metals several times higher than what is obtainable in the environment [15, 16, 17].

The effect of metals in living organisms could be chronic, due to exposures over a long period of time as a result of food chain transfer or acute poisoning due to ingestion or dermal contact [18]. The concentration of heavy metals in the shoot of plants may vary with season as a result of inherent growth dynamics of the plant; metal concentration and its bio-availability in the environment. Data on the response of plants to anthropogenic modification of the environment, particularly in relation to soil and air pollution by heavy metals in northern Nigeria is limited and includes earlier assessments [3, 6, 15, 16] and more recently [19], in which an attempt was made to document the visual symptoms expressed by some ruderal plant species in relation to air pollution as a step towards developing a reference for field identification of pollution events [19].

This study was carried out to determine the spatial and seasonal variations of heavy metal deposition in soils and plants in Nigeria's Sudan Savanna in order to assess the extent of pollution and to identify indigenous plant species that may be pollution tolerant and thus have potential for use in phytorememediation of heavy metal polluted sites.

2. Materials and methods

2.1. Study area

The two sampling sites were located in Katsina State, a state that falls within the Sudan Savanna eco-region of northern Nigeria (See Fig 1).

The Katsina Steel Rolling Mill (See Fig 2) was established in the mid 1970s with an installed capacity of 207, 000 mts per annum [20]

Zobe dam was constructed in 1977 to provide Portable water and for irrigation. It has a storage capacity of 170 Million cubic meters, a surface area of 39.6 km^2 and supports 8137 ha of irrigated land (See Fig 3).

Location/Site	Sampling Stations	Longitude	Latitude	Altitude
Katsina Steel Rolling Mill environs	1	7 37 06. 46 E	12 57 24.72 N	557m
	2	7 37 10. 23 E	12 57 10.23 N	553m
	3	7 37 23.06E	12 57 23.07 N	556m
Zobe Dam catchment	1	7 27 56.40 E	12 21 42. 18 N	510 m
	2	7 27 4.8 E	12 21 19. 12 N	520 m
	3	7 27 52.31 E	12 22 28. 19 N	520 m

Table 1. Geographical Positioning Coordinates of sampling stations at Katsina Steel Rolling Mill environs and Zobe Dam catchment, Katsina state, north Western Nigeria.

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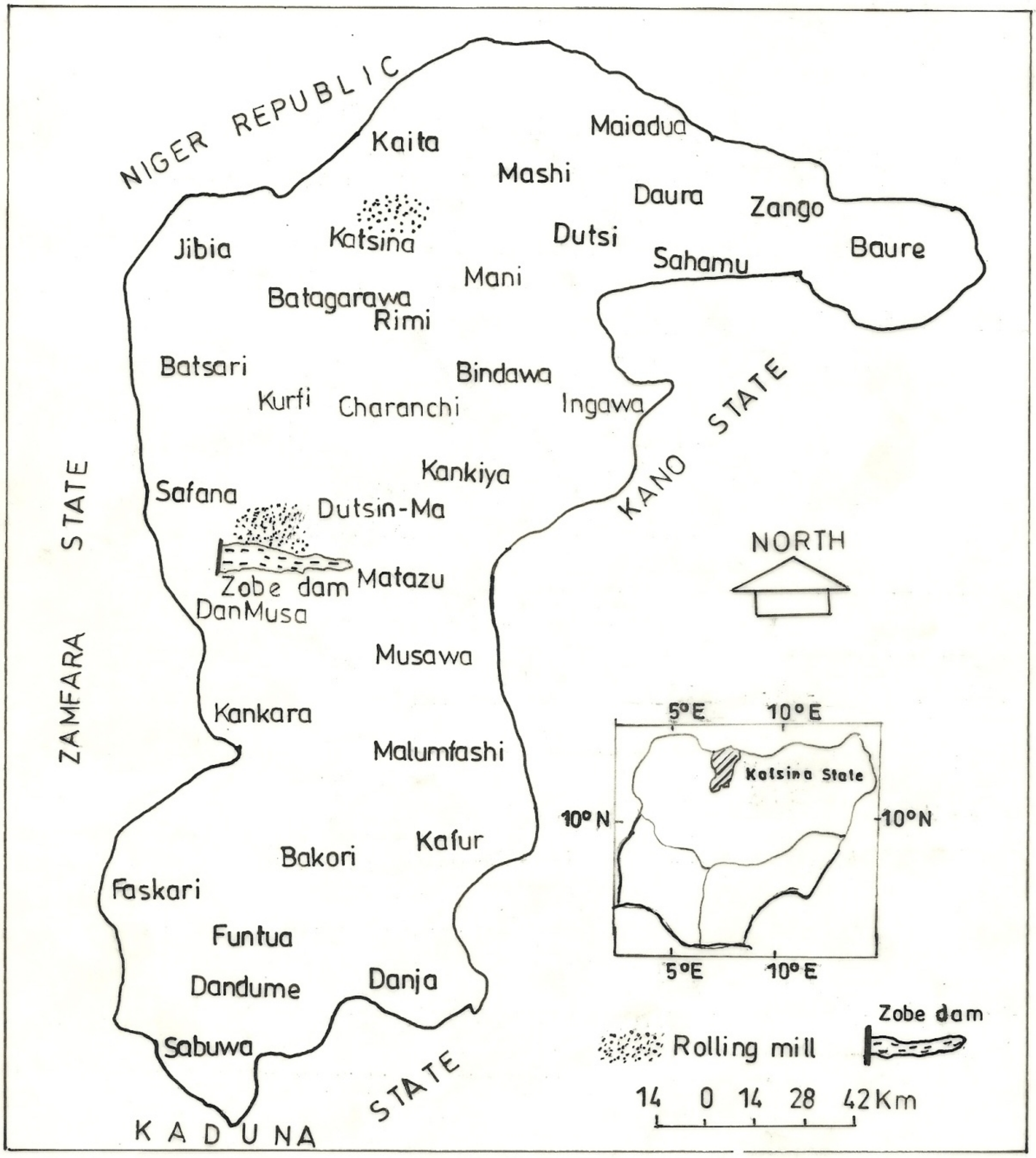

Figure 1. Katsina State, Nigeria showing approximate location of the Steel Rolling Mill and Zobe dam.

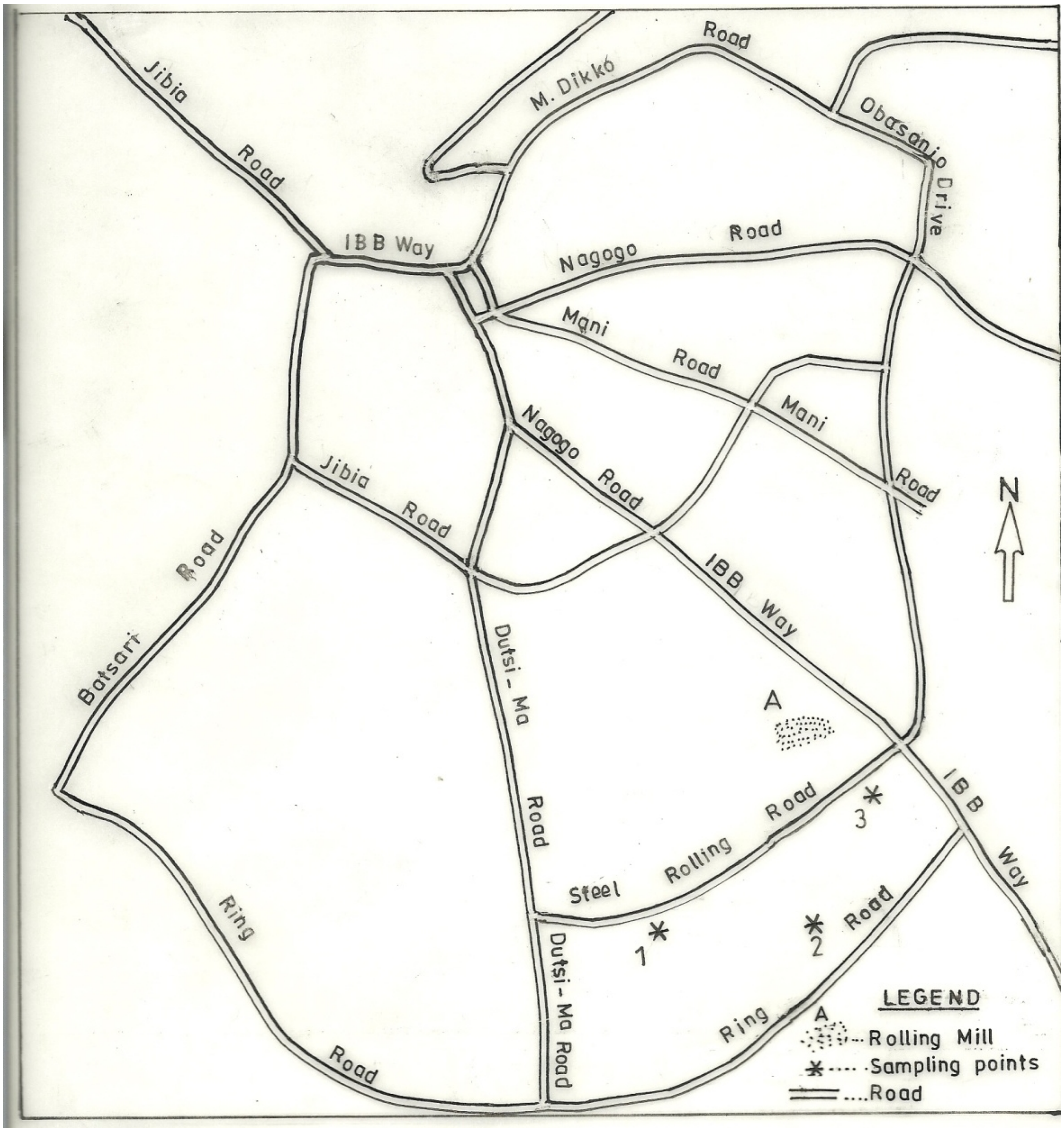

Figure 2. Environs of the Katsina Steel Rolling Mill Showing approximate sampling points.

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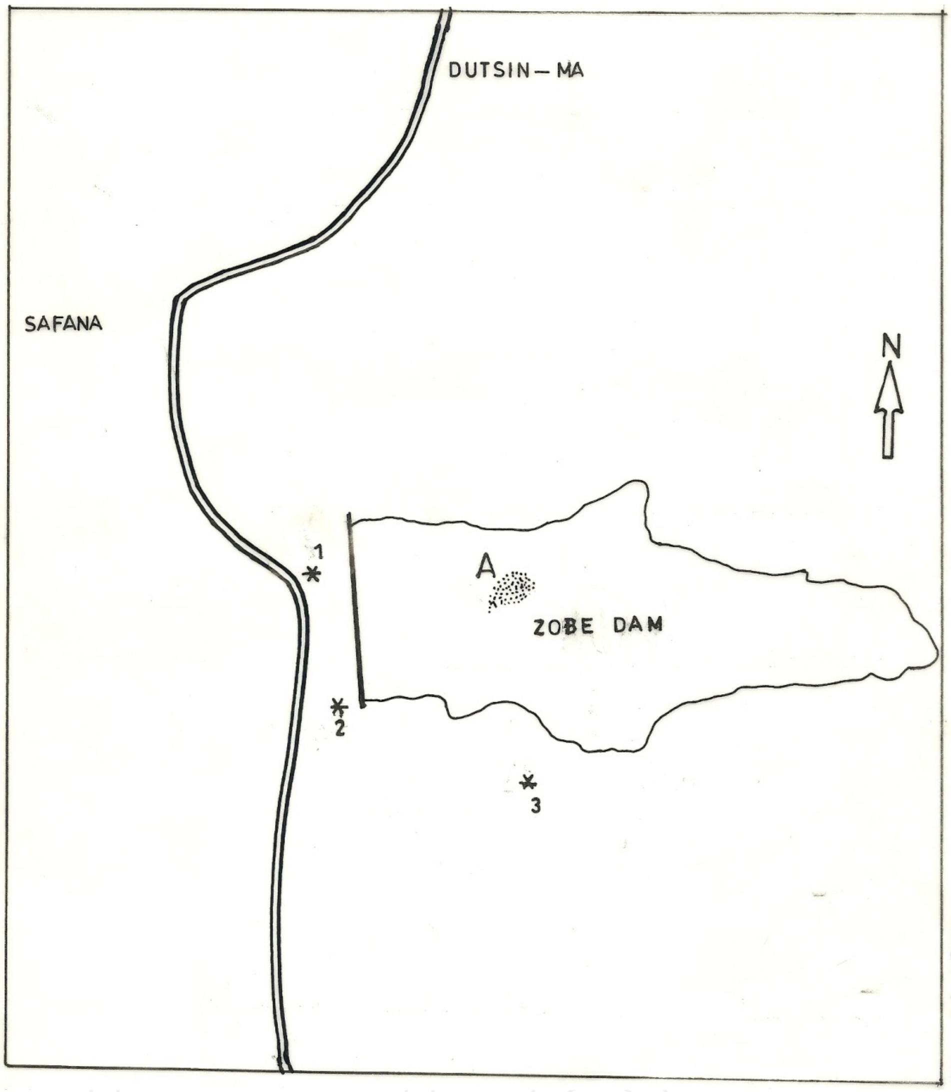

Figure 3. Environs of Zobe Dam showing approximate sampling points

2.2. Sample collection

Soil and plant samples were collected in both dry and wet seasons from three sampling stations per location in 5m by 5m quadrats. Soil samples were collected at 0-15cm depth using a soil auger. The shoot of herbaceous plants with relative abundance greater than five per quadrat, were clipped with a pair of secateurs for heavy metal analysis. Identification of plant samples were confirmed in the herbarium of the Department of Biological Sciences, Ahmadu Bello University, Zaria.

2.3. Sample preparation

Plant samples were washed with tap water and then with distilled water to remove debris and surface contamination. Samples were then bulked and air dried to remove excess moisture. Similarly, samples of the soils collected were bulked into composite samples and air dried for three days (72 hours).

Dried plant and soil samples were ground using a porcelain mortar and pestle and sieved to attain a uniform particle size. Each sample was put in a small transparent polythene bag and labeled.

2.4. Metal analysis

Analysis of the elemental content of the samples was done using the Energy dispersive X-ray fluorescence Spectroscopy (EDXRF) method [21].

The samples were ground manually to powder with an agate mortar and pestle to grain size of less than 125μm. Pellets of 19mm diameter were prepared from 0.3-0.5kg powder mixed with three drops of organic liquid binder and pressed at 10 tons of pressure in a hydraulic press.

Measurements were performed using an annular 25mCi ^{109}Cd as the excitation source, that emits Ag – K rays (22.1 KeV) in which case all elements with lower characteristic excitation energies are accessible for detection in the samples. The system consists furthermore of Si (Li) detector, with a resolution of 170eV for the 5.90KeV line, coupled to a computer controlled ADC – card.

Quantitative analysis of the sample was done using the Emission Transmission (E-T) method and that involves the use of pure target material (Mo) to measure the absorption factors in the sample.

The Mo target served as a source of monochromatic X-rays, which are excited through the sample by primary radiation and then penetrate the samples on the way to the detector. In this way, the absorption factor is experimentally determined which the program uses in the quantification of concentration of the elements. In addition, the contribution to the Mo-K peak intensity by the Zr-K is subtracted for each sample.

Sensitivity calibration of the system was performed using thick pure metal foils (Ti, Fe, Co, N, Zn, Nb, Zr, Mo, Sn, Ta and Pb) and stable chemical compounds (K_2CO_3), $CaCO_3$, Ce_2O_3), WO_3, ThO_2, U_3O_3). The spectra for the samples were collected for 3000s with the ^{109}Cd source and the spectra were then evaluated using the AXIL-QXAS program [22]. ^{109}Cd source was used for the analysis of K, Th, Y, Zr, Nb and Mo.

The accuracy and precision of the measurements was confirmed though an analysis of IAE – V10 (hay powder) and IAEA – 259 (cabbage) certified reference material, distributed by International Atomic Energy Agency (IAEA).

2.5. Bioconcentration factor (Enrichment Coefficient) [23]

This estimates the capacity of plants to accumulate metals, and was computed for each species as:

$$\mathrm{BCF} = \frac{\text{Mean concentration of metal in the plant}}{\text{Mean concentration of metal in the soil}} \tag{1}$$

3. Results

3.1. Metal concentration in soils and plant samples

In the soils around the Zobe dam catchment, the mean concentration of metals generally followed the order Fe>Mn>Zn>Cr>Cu>Ni>Cd and Fe>Mn>Zn>Ni>Cr>Cu>Cd in dry and wet seasons respectively. In soils in the environs of the Katsina Steel Rolling Mill (KTSRM), the mean wet season concentration trend followed the order Fe>Mn>Zn>Cr>Ni>Cu>Cd and Fe>Mn>Zn>Cu>Cr>Ni>Cd in the dry season (Table 2; Fig 4). Differences in soil concentrations of all the metals between seasons were not statistically significant (P=0.05)

3.2. Chromium

The soil around the Zobe dam catchment had a mean Cr concentration of 66.00 mg/kg and 70.53 mg/kg, in dry and wet seasons respectively (Table 2; Fig 4). The mean Cr concentration in the environs of the Katsina Steel Rolling Mill was 46.67 mg/kg in the dry season and 70.53mg/kg in the wet season. The wet season concentrations were observed to be higher than acceptable limits for soils in Canada and the Netherlands (Table 3).

Sampling Locations	Seasons and P Values	Metals						
		Cr	Cu	Ni	Cd	Fe	Mn	Zn
Zobe Dam	DRY	66.00	29.66	26.87	0.15	22700.00	360.58	263.33
	WET	70.53	7.92	184.57	1.05	55516.93	891.66	428.45
	P value	0.13ns	0.33ns	0.64ns	0.29ns	0.25ns	0.33ns	0.34ns
KTSRM	DRY	46.67	56.91	46.31	0.33	18266.67	277.22	693.67
	WET	69.58	12.05	84.50	0.00	58867.00	745.75	385.00
	P value	0.23ns	0.60ns	0.12ns		0.32ns	0.17ns	0.94ns

Differences in soil heavy metal content were not significant (ns) between seasons in both locations.

Table 2. Mean Seasonal Heavy Metal Concentration (mg/kg) and T-test P-values of Soils collected from Zobe dam catchment and the environs of Katsina Steel Rolling Mill (KTSRM)

Recommending Agency/Country		Cr	Cu	Ni	Cd	Fe	Mn	Zn
WHO [24]		100	30	80	NA	NA	NA	200
Mexico (Agricultural soils) [25]		NA	NA	1600.00	37.00	NA	NA	NA
USA [26]		3, 000	4, 300	75.00		NA	NA	7500
Japanese MOE [27]		250	NA	NA	150	NA	NA	NA
Canadian CCME [28]	**Agriculture**	64	63	50	14	NA	NA	NA
	Residential/Park	64	63	50	10	NA	NA	NA
	Commercial	87	91	50	22	NA	NA	NA
	Industrial	87	91	50	22	NA	NA	NA
Austria [29]		100	60 to 100	50 t0 70	1 to 2	NA	NA	NA
Germany [29]		60	40	50	1	NA	NA	NA
France [29]		150	100	50	2	NA	NA	NA
Luxembourg [29]		100-200	50 to 140	30 to 75	1 to3	NA	NA	NA
Netherlands [29]		30	40	15	0.5	NA	NA	NA
Sweden [29]		60	40	30	0.4	NA	NA	NA
United Kingdom [29]		400	135	75	3	NA	NA	NA

NA — Not available

Table 3. International Recommended Levels of Heavy Metals in Soils (mg/kg)

In the plant samples, the highest concentration of Cr was recorded in *Senna siberiana* (2.64 mg/kg) in the dry season and *Englerina gralicinus* and *Terminalia mollis* (3.30 mg/kg) in the wet season (Fig 5). "Normal" concentration of Cr in plants is described as being from 0.1 to 0.5 mg/kg, while concentrations between 5 to 30 mg/kg as "Excessive" and 75 to 100 mg/kg, "Phytotoxic" (Table 4).

3.3. Copper

Mean concentrations of Cu in the soil samples collected around the Zobe dam catchment was 29.66mg/kg in the dry season and 7.92 mg/kg in the wet season. Around the environs of KTSRM, the mean Cu concentration was observed to be 56.91 mg/kg in the dry season and 12.05 mg/kg in the wet season (Table 2; Fig 4). Only soil samples collected from the environs of KTSRM in the dry season were observed to have mean Cu concentration above the acceptable limits of the WHO (30 mg/kg), Germany, the Netherlands and Sweden (40 mg/kg) Table 3).

In plant samples collected, the highest concentration of Cu was observed in members of the genus *Diospyros, D. piscatoria*, 10.41 mg/kg and *D. mespiliformis* 10.40 mg/kg in the dry season. In the wet season, the concentration of Cu was generally higher in the plants, with the highest concentration recorded in *Combretum mucronatum* (34.58 mg/kg) (Fig 5). Concentrations between 20 to 100 mg/kg in plants have been described as being excessive (Table 4).

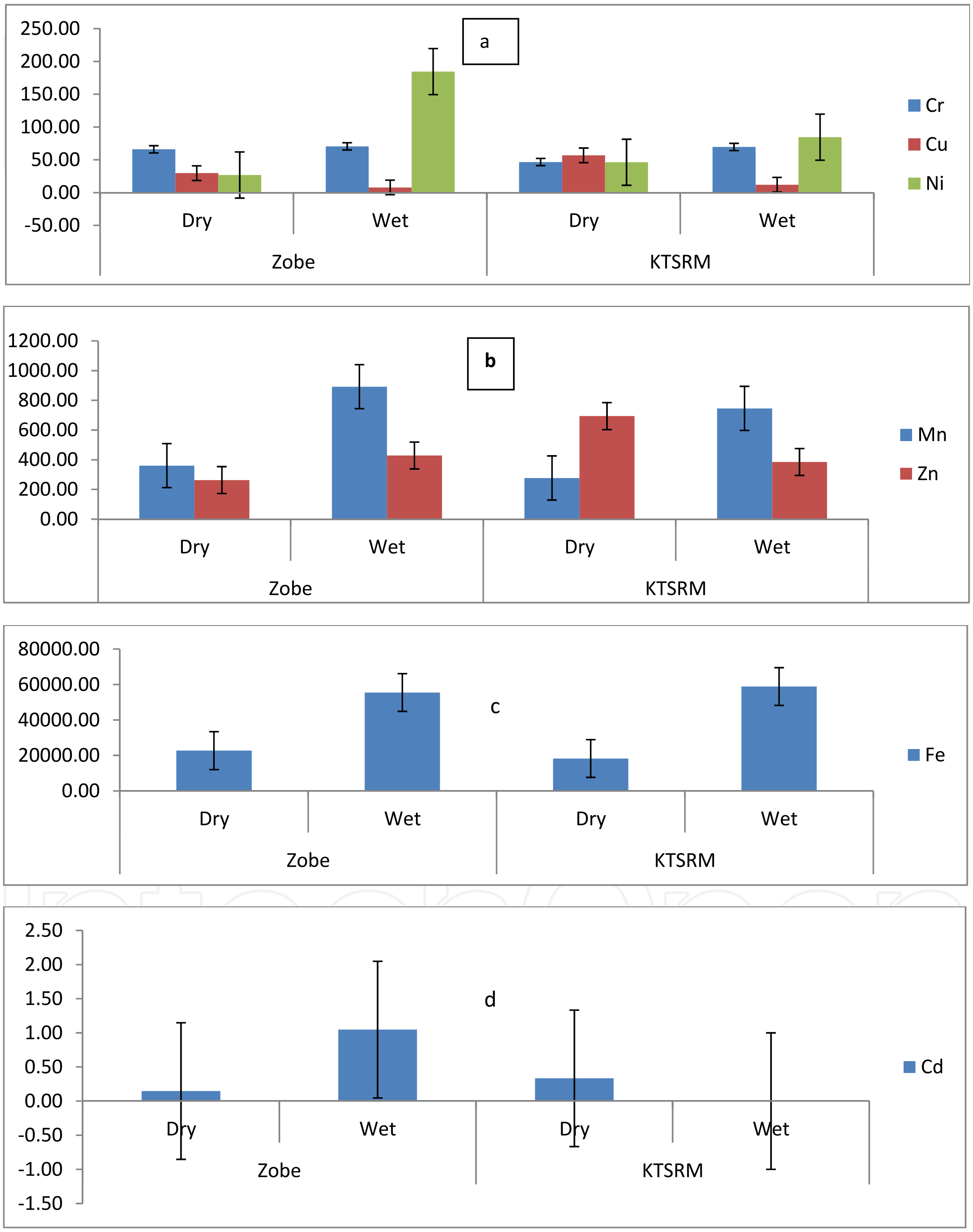

Figure 4. Seasonal variation in heavy metal concentration (mg/kg) in soils of Zobe dam catchment and the environs of Katsina Steel Rolling Mill (KTSRM)(a, Cu, Cr and Ni; b, Mn and Zn; c, Fe; and d, Cd).

	NORMAL	DEFICIENCY	EXCESSIVE	PHYTOTOXIC
Cd	NA	NA	NA	5 to 30
Zn	27-150	10 to20	100 to 400	70 to 400
Cr	0.1- 0.5	NA	5 to 30	75-100
Cu	5.1-30	2 to 5	20-100	60-125
Ni	0.1 -5	NA	10-100	100

Table 4. Range Values of Heavy Metals in Vegetation (mg/kg)

3.4. Nickel

In soils around the Zobe dam catchment, the mean Ni concentration was 184.57 mg/kg in the wet season and 26.87 mg/kg in the dry season. Whereas mean concentrations of Ni of 46.31 mg/kg and 84.50. mg/kg were observed in dry and wet seasons respectively, in soils around the environs of the KTSRM (Table 2; Fig 4). The mean concentration of Ni in both sites were observed to be higher than the acceptable limits of WHO (80 mg/kg), USA (75 mg/kg), Canada, France and Germany (50 mg/kg), Austria (50 to 70 mg/kg), Luxembourg (30-75 mg/kg); and Netherlands, Sweden and the UK (Table 3).

In plant samples, *Senna siberiana* had the highest Ni concentrations of 3.69 mg/kg and 13.77 mg/kg in dry and wet seasons respectively in the environs of KSTRM. *Diospyros piscatoria* was observed to have the highest concentration of 2.20 mg/kg for Ni in the dry season while *Ipomoea ascarafolia* had the highest concentration of 3.63 mg/kg among plants collected in the wet season around the Zobe dam catchment (Fig 5). Normal concentration of Ni in plants has been described to be between 0.1 to 5 mg/kg, whereas concentrations between 10 to 100 mg/kg as excessive (Table 4).

3.5. Cadmium

Soils around the Zobe dam catchment had a mean Cd concentration of 0.15 mg/kg in the dry season and 0.33 mg/kg in the wet season. In the environs of KTSRM, a mean concentration of 1.05 mg/kg was observed in the dry season. In the wet season Cd concentrations were below detectable limits in the wet season (Table 2; Fig 4). The above mean concentrations were found to be within the acceptable limits of the WHO and the Countries listed in Table 3.

Ipomoeaascarafolia had the highest concentration of cadmium in dry (3.90 mg/kg) and wet (1.03 mg/kg) seasons among plants sampled around the Zobe dam catchment. In the environs of KTSRM, *Ziziphus abyssinica* was observed to have the highest concentration of 4.5 mg/kg of Cd in the dry season, while in the wet season *Cadaba farinosa* was observed to have the highest concentration of 0.54 mg/kg (Fig 5).

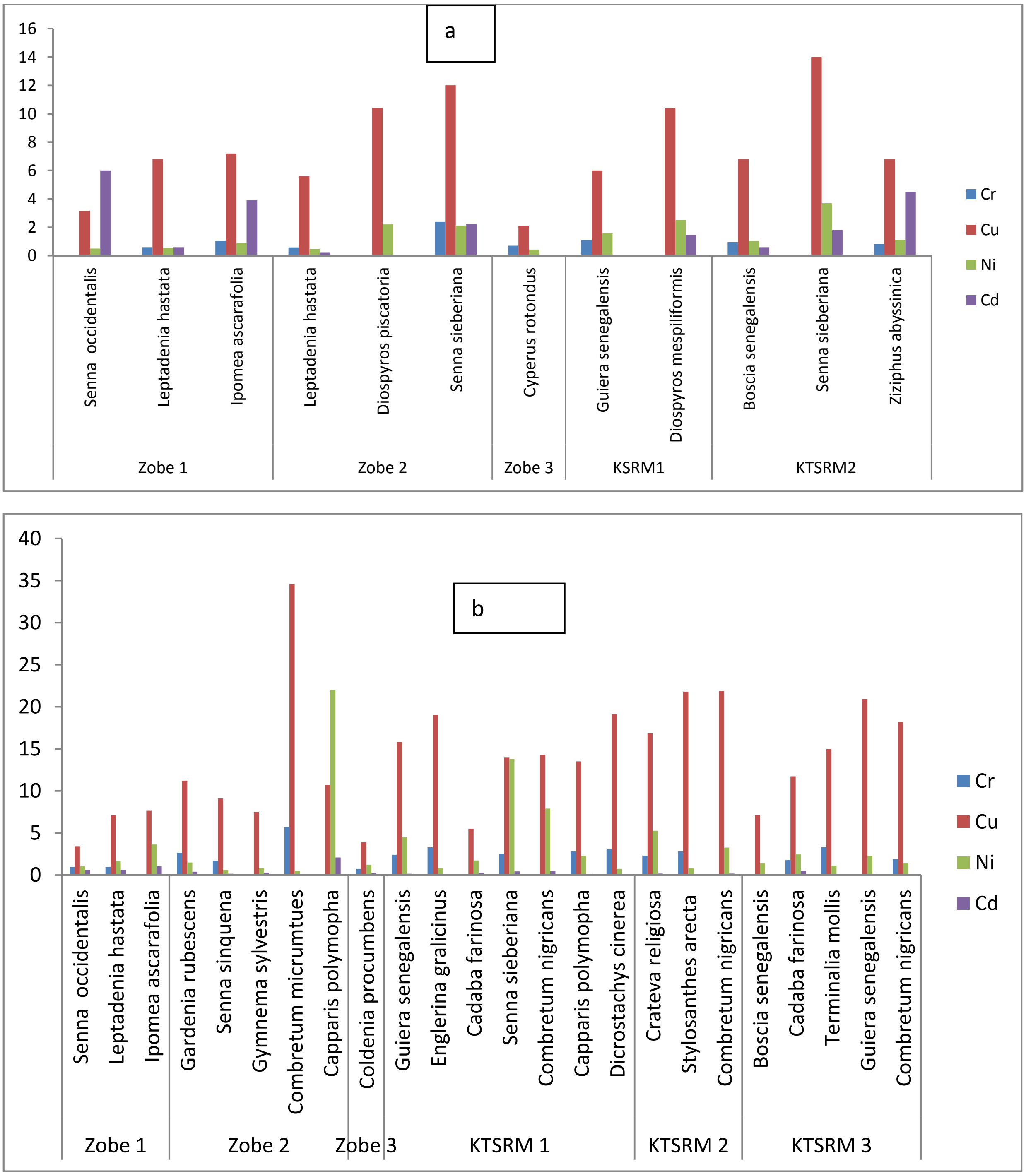

Figure 5. Concentration (mg/kg) of Cr, Cu, Ni and Cd in plants collected from Zobe Dam catchment and the environs of Katsina Steel Rolling Mill (KTSRM) during the Dry (a) and Wet (b) Seasons

3.6. Iron

Soils in the two study sites were observed to have a higher concentration of Fe in the dry season than in the wet season. Soils from Zobe dam catchment and the environs of KTSRM had means of 22, 700 and 555, 16.93 mg/kg; and 18, 266.67 and 58867 mg/kg in dry and wet seasons, respectively (Table 2; Fig 4).

Soil samples collected in the wet season were observed to have a higher concentration of Fe (891.66 and 745.75 mg/kg in Zobe dam catchment and the environs of KTSRM, respectively) than the dry season (360.58 and 277.22 mg/kg in Zobe dam catchment and environs of KTSRM, respectively (Table 2; Fig 4).

Plant species with the highest concentration of Fe in the wet season were *Ipomoea ascarafolia* (115.50 mg/kg) and *Guiera senegalensis* (264.10 mg/kg) for Zobe dam catchment and environs of KTSRM, respectively. In the dry season, *Coldenia procumbens* (184.00 mg/kg) and *Guiera senegalensis* (176.84 mg/kg) were observed to have the highest concentration of Fe Zobe dam catchment and the environs of KTSRM, respectively (Fig 6).

3.7. Manganese

The mean concentration of Manganese in soils was observed to be higher in the wet season (891.66 and 745.75mg/kg) than in the dry season (360.66 and 277mg/kg) for Zobe dam catchment and KTSRM respectively.

In plants, *Diospyros piscatoria* (36.5 mg/kg) and *Boscia senegalensis* (102.87 mg/kg) were observed to have the highest Mn concentration during the dry season in Zobe dam catchment and environs of KTSRM, respectively. In the wet season, *Capparis polymopha (*syn. *C. tomentosa)* (80.72 mg/kg) and *Senna siberiana* (190.60 mg/kg) were observed to have the highest concentration of Mn in Zobe reservoir and KTSRM, respectively (Fig 6).

3.8. Zinc

Zn concentrations in soils showed a similar pattern with Mn and Fe in Zobe dam catchment during the dry season, being higher in the wet (428.45 mg/kg) than the dry season (263.67 mg/kg). A reversed trend was observed in the environs of KTSRM, with the concentration being higher in the dry season (693.67 mg/kg) than the wet season (385.00 mg/kg) (Table 2; Fig 4). These observed mean concentrations of Zn were higher than the 200 mg/kg acceptable limit of the WHO.

Leptadeniahastata (38.5 mg/kg), *Senna siberiana* (54.84 mg/kg) were observed to have the highest concentration of Zn in the dry season for Zobe dam catchment and the environs of KTSRM, respectively. In the wet season, the highest concentrations of Zn in plant samples were presented by *Capparis polymopha (*syn. *C. tomentosa)* (158.50 mg/kg) and *Senna siberiana* (132.60 mg/kg) (Fig 6). Normal concentrations of Zinc in plants fall between 27 to 150 mg/kg. However, concentrations between 100 to 400 mg/kg may be considered Excessive, while from 70 to 400 mg/kg, as Phytotoxic (Table 4). This is dependent on the plant species in question.

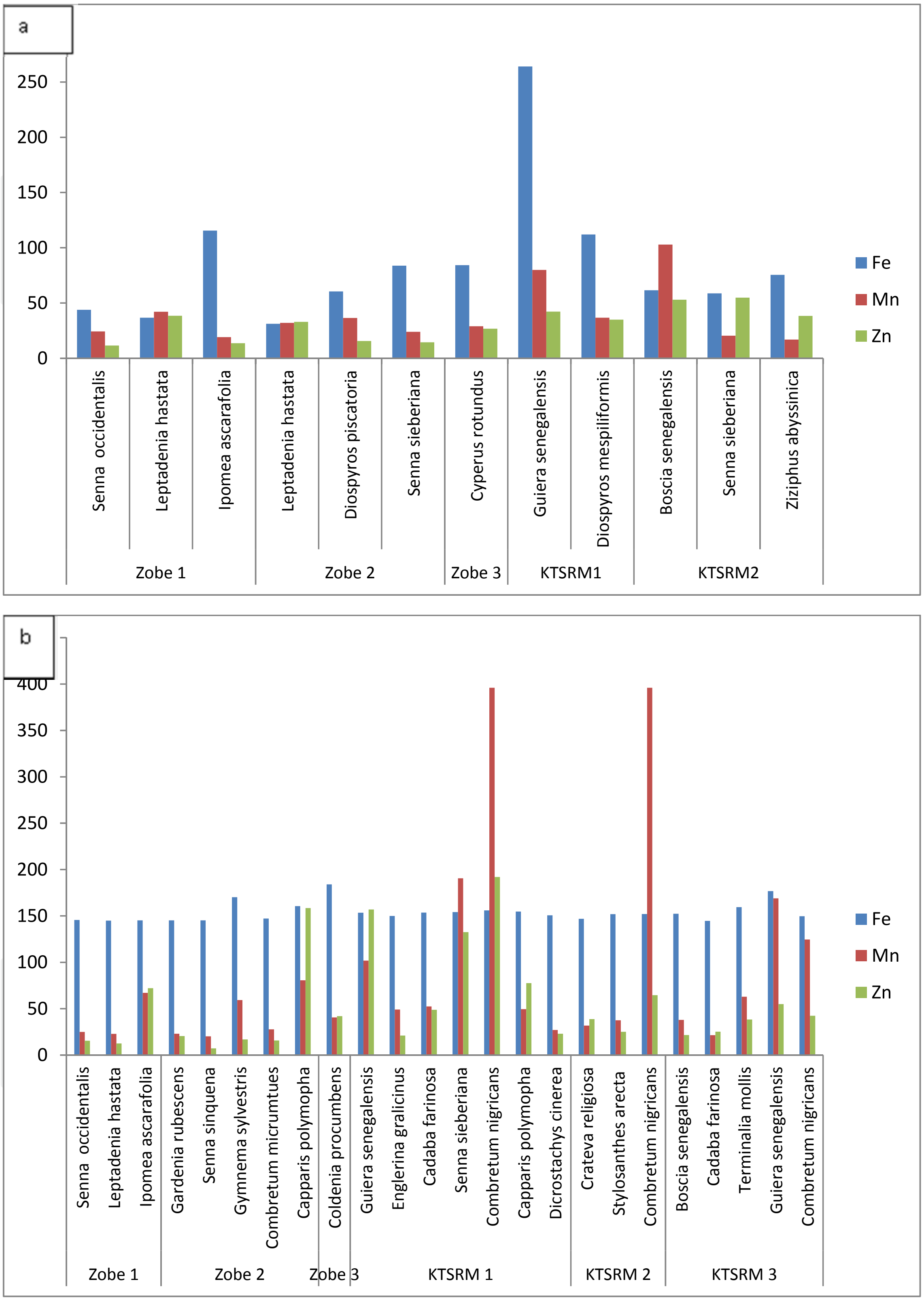

Figure 6. Concentration (mg/kg) of Fe, Mn and Zn in plants collected from Zobe dam catchment and the environs of Katsina Steel Rolling Mill (KTSRM) and the Dry (a) and Wet (b) Seasons

4. Bioconcentration Factor (BCF) of heavy metals in plants

Chromium: BCF for Cr was generally low across seasons and site. In the two study areas, the BCF of Cr ranged between 0.00 to 0.03 in the dry season, while in the wet season it varied between 0.00 and 0.07. *Combretummucronatum* was observed to have the highest BF value (Fig. 7and 8).

Copper: BCF for Cu (Fig. 7 and 8) was generally higher in the wet season than in the dry season, with *Combretum mucronatum* having the highest value of 6.16. *Ipomoea ascarafolia* was observed to have the highest BF in the dry season. Across seasons and sites, other plant species that had BCF >1.0, were: *Gardenia rubescens*, *Senna singuena*, *Gymnema sylvestris*, *Capparis polymopha*, *Guiera senegalensis*, *Englerina gracilinus*, *Senna siberiana*, *Combretum nigricans*, *Dicrostachys cinerea*, *Crateva religiosa*, *Stylosanthes arectalea* and *Terminalia mollis* (Fig. 7 and 8).

Nickel: Highest BCF of Ni was observed in *Combretumnigricans* (1.61) and *Capparis polymopha (*syn*. C. tomentosa)* (0.61). Most plants show a higher BF during the wet season in comparison to the dry season (Fig. 7 and 8).

Iron: BCF of Fe was generally low, with the highest value of 0.07 observed in *Sennasiberiana*, across seasons and sites (Fig. 7 and 8).

Manganese: For Manganese, BCF was generally low (<1.0) (Fig. 9) across seasons and sites. In the wet season, *Combretum nigricans* was observed to show a high BF of 0.53 and 0.41 of Mn in two different replicate plots. *Guiera senegalensis* was observed to accumulate Mn to a BF of 0.38. *Boscia senegalensis* was observed to have a BF of 0.62 during the dry season (Fig. 7 and 8).

Zinc: For Zinc, BCF was also generally low (<1.0) (Fig. 9) across seasons and sites.The highest BCF of Zn were observed in Ipomoea ascarafolia (0.70), Capparis polymopha (syn. C. tomentosa) (0.59), Guiera senegalensis (0.41) and Combretum nigricans (0.50) (Fig. 7 and 8).

Cadmium: *Sennaoccidentalis* and *Ipomoea ascarafolia* were observed to have considerably high BCF of 20.69 and 13.45 respectively. Most of the other plants were observed to have recorded higher BF in the wet season than the dry season. Across sites and seasons, other species that had BCF >1.0, were *Leptadenia hastata*, *Capparis polymopha*, *Senna siberiana* and *Ziziphus abyssinica* (Fig. 9)

Table 5 presents a summary of the most frequently accumulated metal in all species encountered at the sampling locations. Eighteen plant species were found to bioaccumulate metals (BCF >1) in their above ground part to varying degrees. Cu was the most frequently accumulated, being found to occur in all of the 18 species (100%) across sites and seasons. This was followed by Cd in 6 species (33.33%) and Ni in only one (05.6%) species.

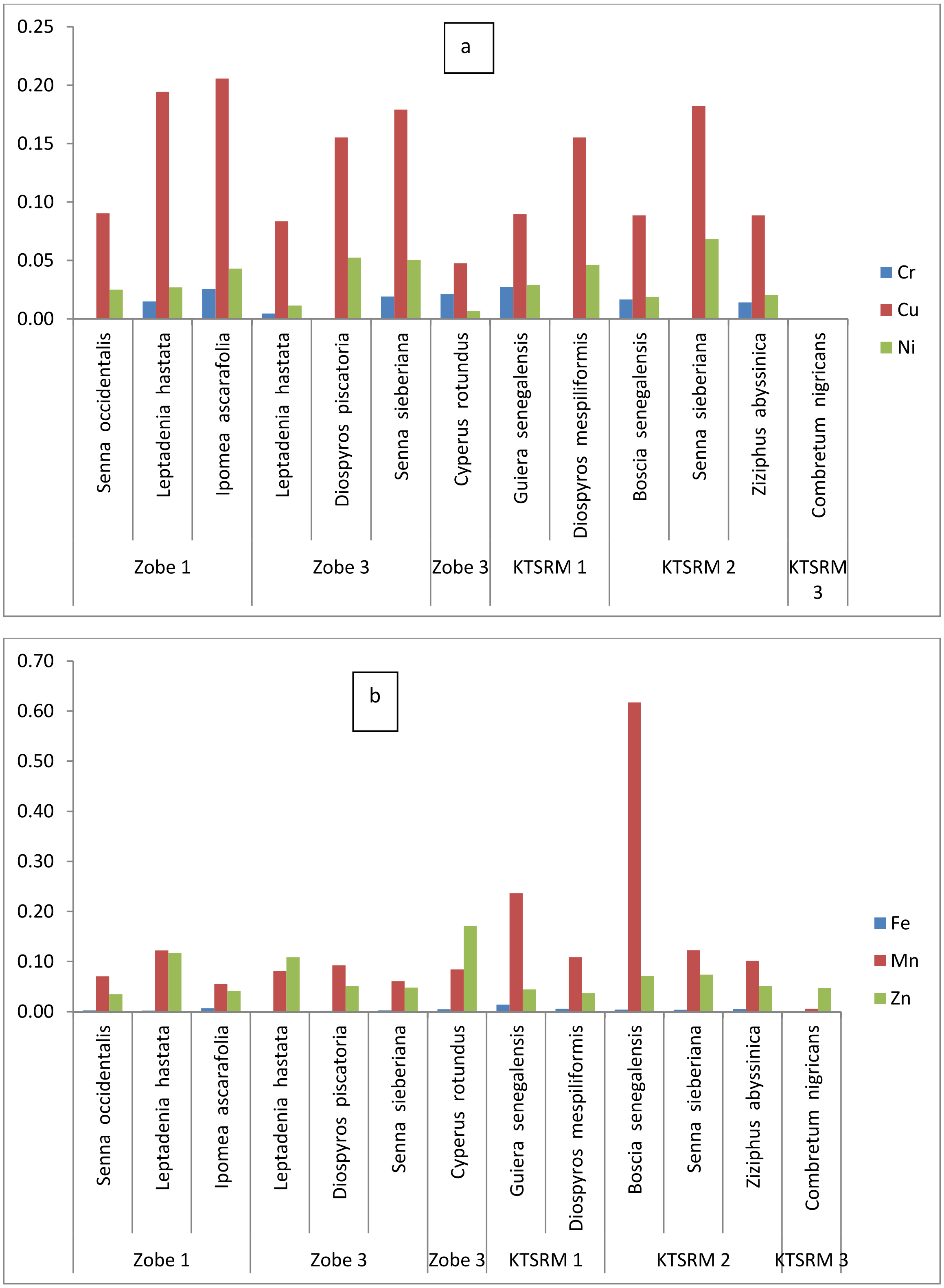

Figure 7. Bioconcentration of (a) Cr, Cu and Ni, (b) Fe, Mn and Zn in plants collected from Zobe dam catchment and the environs of Katsina Steel Rolling Mill during the Dry Season

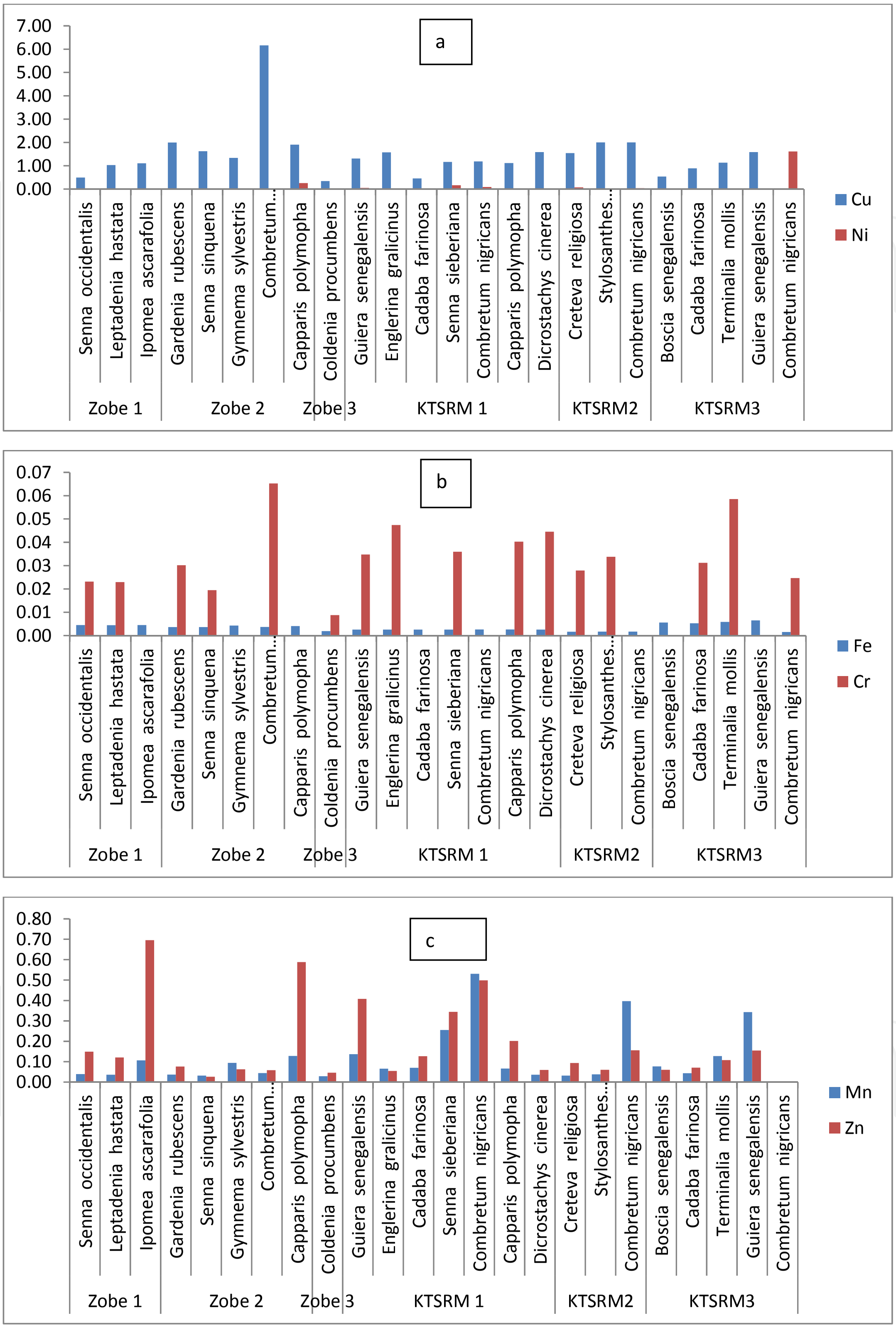

Figure 8. Bioconcentration of (a) Cu and Ni, (b) Fe and Cr, and (c) Mn and Zn in plants collected from Zobe dam catchment and the environs of Katsina Steel Rolling Mill during the Wet Season

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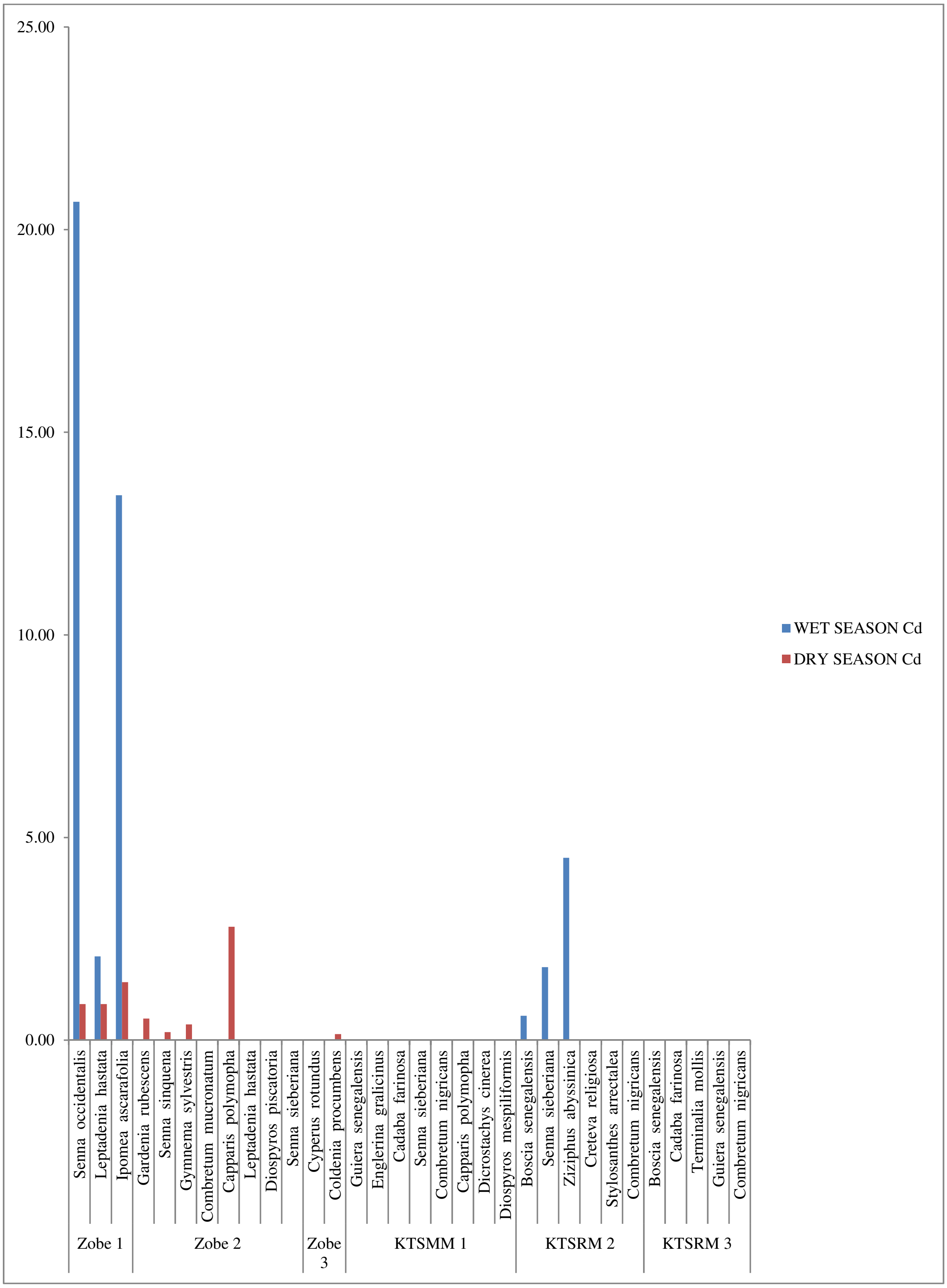

Figure 9. Bioconcentration of Cd in plants collected from Zobe dam catchment and the environs of Katsina Steel Rolling Mill during the Wet and Dry Seasons

S/No.	Family	Plant Species	Frequency of Occurrence (%)				Phtoextractive potential (as function of BCF)					
			Zobe Dam		KTSRM		Cu		Ni		Cd	
			Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
1	Caesalpiniaceae	*Sennaoccidentalis*	0	33	0	0	-	-	-	-	-	+
2	**Asclepiadaceae**	*Leptadeniahastata*	33	67	0	0	+	-	-	-	-	+
3	Convolvulaceae	*Ipomeaascarafolia*	33	33	0	0	+	-	-	-	+	+
4	Rubiaceae	*Gardeniarubescens*	33	0	0	0	+	-	-	-	-	-
5	Caesalpiniaceae	*Sennasinguena*	0	33	0	0	+	-	-	-	-	-
6	**Asclepiadaceae**	*Gymnemasylvestre*	33	0	0	0	+	-	-	-	-	-
7	Combretaceae	*Combretummucronatum*	33	0	0	0	+	-	-	-	-	-
8	Capparidaceae	*Capparispolymopha*	33	0	0	0	+	-	-	-	+	-
9	Caesalpiniaceae	*Sennasieberiana*	0	33	0	0	+	-	-	-	-	-
10	Combretaceae	*Guierasenegalensis*	0	0	66	33	+	-	-	-	-	-
11	Loranthaceae	*Englerinagralicinus*	0	0	33	0	+	-	-	-	-	-
12	Combretaceae	*Combretumnigricans*	0	0	100	0	+	-	+	-	-	-
13	Mimosaceae	*Dicrostachyscinerea*	0	0	33	0	+	-	-	-	-	-
14	Caesalpiniaceae	*Sennasieberiana*	0	0	33	33	+	-	-	-	-	+
15	**Rhamnaceae**	*Ziziphusabyssinica*	0	0	0	33	-	-	-	-	-	+
16	Capparidaceae	*Cratevareligiosa*	0	0	33	0	+	-	-	-	-	-
17	Papilionaceae	*Stylosanthesarectalea*	0	0	33	0	+	-	-	-	-	-
18	Combretaceae	*Terminaliamollis*	0	0	33	0	+	-	-	-	-	-

(+) = BCF > 1; (-) = BCF < 1

Table 5. Seasonal occurrence of plant species with potential for phytoextraction (BCF) of Cu; Ni and Cd in the catchment of Zobe Dam and the environs of Katsina Steel Rolling Mill.

5. Discussion

Concentrations of heavy metals in soils were generally observed to be higher during the wet season in both locations although the differences were not statistically significant (P=0.05). This differs somewhat with the findings of [30], who observed a higher concentration of these metals in the dry season than the wet season. Seasonal variations in patterns of metal deposition could be related to the intensity and duration of climatic variables such as precipitation, temperature etc., that interface with topography, drainage, soil structure/texture etc., to determine the physicochemical properties of the soil in a particular location. Soil physicochemical properties have complex, interdependent effects on metal solubility, with the most important of these including solution composition (inorganic and organic solubles), Eh, and pH; type and density of charge on soil colloids; and reactive surface area, that interact with factors like metal concentration and form, particle size distribution, quantity and reactivity of hydrous oxides, mineralogy, degree of aeration and microbial activity [31]. The aggregate effects of these complex interactions determine the bioavailabilty of metals to plants.

The above acceptable limits of the observed concentrations of Cr, Cd, Cu, Ni and Zn may be attributed to some of the human activities (mainly agriculture and industrial) going on around the sites. This presents health risks to humans and other animals as the metals contaminate both aquatic and terrestrial ecosystems. Above background values of these metals may have resulted from metal smelting and electroplating activities, burning of fossil fuels, application of phosphate fertilizers, disposal of solid wastes, and quarry activities [32, 33, 34, 35]. High levels of heavy metals in terrestrial or aquatic ecosystems ultimately end up being transmitted and accumulated in the food chain. Health risks to humans arise when metal polluted water is used as drinking water or when animals that have consumed vegetative materials in which metals have accumulated, are used for food. Furthermore, cultivation of crops on metal polluted soils indicates a possibility of consuming crops in which metals have accumulated. Although, specific effects of the various metals on human health have been discussed by several authors, the biotoxic effects of metals to humans have generally been outlined as ranging from gastrointestinal disorders, diarrhoea, stomatitis, tremor, hemoglobinuria, ataxia, paralysis, vomiting and convulsion, depression, coughing and wheezing, respiratory inflammation, dermatitis, leukocytis, low blood pressure, jaundice haemolytic anemia pneumonia and coma to death (Cd, Pb, As, Hg, Zn, Cu, Cr, Ni and Al). The nature of these effects could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic. For example, see [15, 16, 40, 41, 42].

Concentration of Cr in all the plants observed was found to be below the 5 to 30 mg/kg described as phytotoxic to plants [35, 36]. The excessive to phytotoxic concentrations of Zn in *Capparis polymopha* (syn. *C. tomentosa*) and *Guiera senegalensis*; Cd in *Senna occidentalis;* Ni in *Senna siberiana* and Cu in *Combretum mucronatum*, may be a consequence of the high values observed in the soils or direct deposition from the atmosphere. In addition to soil concentrations of metals, other factors that determine the uptake, translocation and accumulation of metals in plants include soil pH, cation exchange capacity, organic matter content, soil texture and interaction with other metals, as well as translocation factor (rate of movement of metals between root and shoot tissues) for the particular metal [43, 44]. Heavy metals in toxic concentrations within the plant have inhibitory effects on enzymatic activity, stomatal function, photosynthesis and nutrient uptake, which may be expressed visually as chlorosis, reduced/stunted growth and yield depression. Plants vary widely in their ability to tolerate high concentrations of metals in their tissues. This variation is usually natural and dependent on inherent genetic factors. The genetic disposition confers the ability to employ a range of avoidance/exclusion or detoxification mechanisms that enable the plants cope with high metal loads. These may include the binding of metals (e.g. Ni and Cr) with amino acids, peptides and organic acids to form low molecular weight compounds, formation of phytochelatins, by binding (e.g. Cu and Pb) with sulphur-rich proteins and cellular adaptations. Other strategies may involve roles for mychorrhizas, the cell wall, extra-cellular exudates, efflux pumping mechanisms in the plasma membrane and formation of stress proteins etc [3, 45, 46, 47].

Plants with BCF of metals >1.0, have been described as suitable for phytoextraction [37, 38]. Some of the plants observed in this study with this potential include; *Combretum mucronatum, Ipomoea ascarafolia, Gardenia rubescens*, *Senna singuena*, *Gymnema sylvestre*, *Capparis polymopha* (syn. *C. tomentosa*), *Guiera senegalensis*, *Englerina gracilinus*, *Senna siberiana*, *Combretum nigricans*, *Dicrostachys cinerea*, *Crateva religiosa*, *Stylosanthes arectalea* and *Terminalia mollis* for Cu; *Senna occidentalis*, *Ipomoea ascarafolia*, *Leptadenia hastata*, *Capparis polymopha* (syn. *C. tomentosa*), *Senna siberiana* and *Ziziphus abyssinica* for Cd; *Combretum nigricans* for Ni. The ability of these plants to concentrate high levels of these metals suggests that they may have a good potential for phytoremediation.

No hyper-accumulator was observed in this study. Hyper-accumulators are plants that can accumulate at least 0.1% wt of Cu, Cd, Cr, Pb, Ni and Co or 1% wt of Zn and Mn [39]. There are possibilities for genetic modification of plants to enhance their capacity for metal tolerance [48].

6. Recommendations for further research

There is a great need to establish environmentally safe limits for metals in plant and soils of the various eco-regions in Nigeria. This need is emphasized by the observed variations in published background values from one country to another and even within the same country. These background values are often dependent on the geological history of the area. A comparison of observed field values with national recommended levels for heavy metals, developed from the background values will give a more realistic assessment of the pollution status. Furthermore, the search for alternative green technology that can be employed in remediation of pollution events must necessarily be a continuous one, due to the relative low cost and environmental friendliness of this option as compared to others. In this regard, ruderal species rather than those with agricultural value must be the candidates of choice for avoidance of obvious conflicts. The species that have indicated potentials for phytoextraction of Cu, Cd and Ni in this research may therefore be further evaluated.

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7. Conclusion

The concentrations of Cr, Cu, Ni and Zn in soils around the Zobe dam catchment and the environs of Katsina Steel Rolling Mill were found to be above the acceptable limits. This presents health risks to humans and other animals as the metals contaminate both aquatic and terrestrial ecosystems.

Although no hyper accumulator plant species was encountered in this study, eighteen (18) plant species were identified to have high bioconcentration of metals, which indicated tolerance to excessive or phytotoxic metal concentrations. In addition, they generally produce high above ground biomass, due to rapid vegetative growth. These plants include: *Combretum mucronatum, Ipomoea ascarafolia, Gardenia rubescens*, *Senna singuena*, *Gymnema sylvestre*, *Capparis polymopha* (syn. *C. tomentos*a), Guiera senegalensis, Englerina gracilinus, Senna siberiana, Combretum nigricans, Dicrostachys cinerea, Crateva religiosa, Stylosanthes arectalea, Terminalia mollis, Senna occidentalis, Leptadenia hastata, and Ziziphus abyssinica. These present further possibilities for evaluating metal tolerance in relation to their potential use in phytoremediation programmes in metal polluted sites.

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